Photoinduced Electron Transfer and Its Applications

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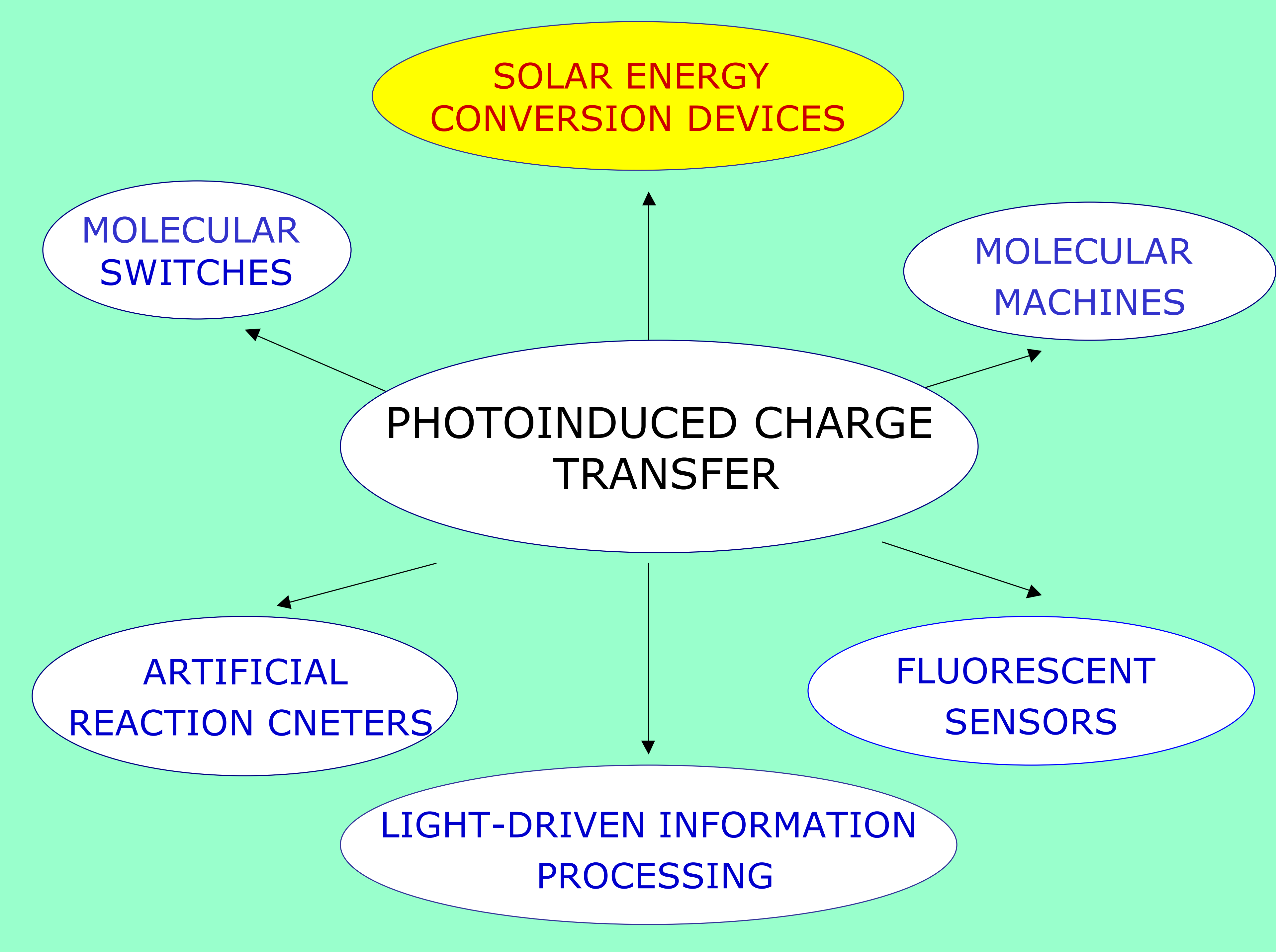
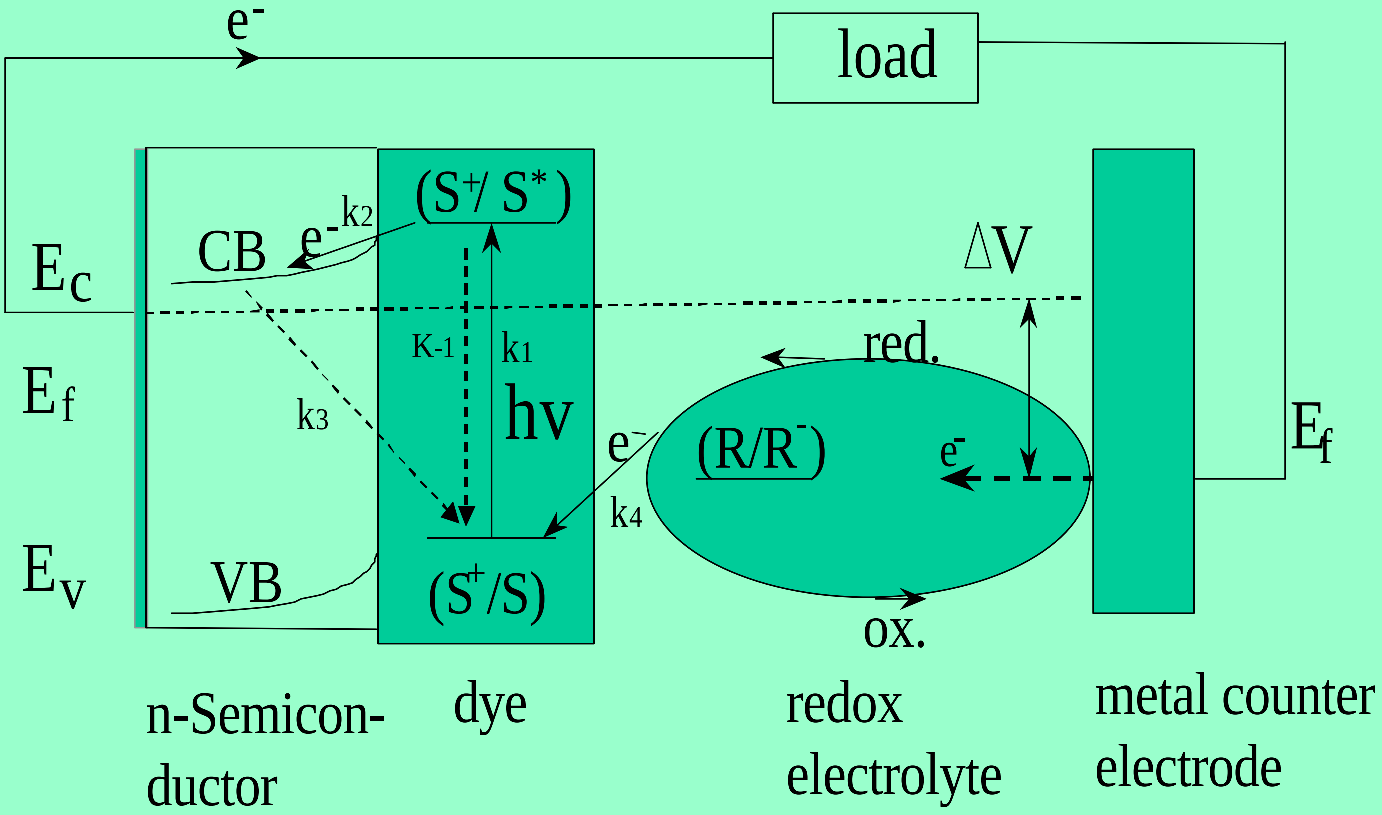

SOLAR ENERGY CONVERSION DEVICES
MOLECULAR SWITCHES
MOLECULAR MACHINES
PHOTOINDUCED CHARGE TRANSFER
ARTIFICIAL REACTION CNETERS
FLUORESCENT SENSORS
LIGHT-DRIVEN INFORMATION PROCESSING

Principle of the nanocrystalline electrochemical solar cell



Factors of Affecting the Performance of Dye-sensitized Solar Cells

- chemical, redox and photophysical and photochemical properties of the dye
- Structure, morphology optical and electrical properties of the nanoporous oxide layer
- visco-elastic and electrical properties of the electrolyte carrying the redox mediator
- electrical and optical properties of the counter electrode

Quantitative assessment of the solar cell performance

- IPCE:incident photon-to-current conversion efficiency for monochromatic radiation

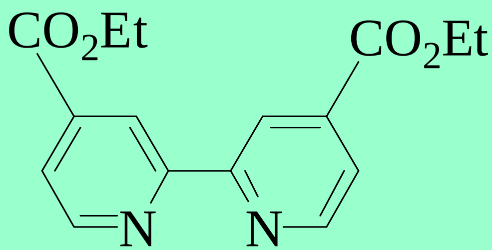
- η_{eff}:overall white light-to-electrical conversion efficiency

Requirements for Efficient Sensitizers

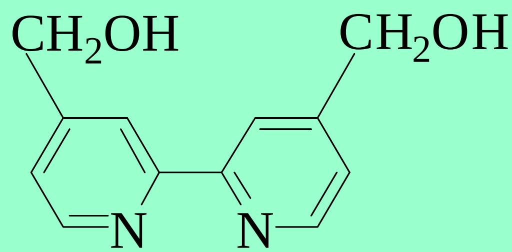
- ✐ **high stability in the oxidized, ground, and excited states**
- ✐ **suitable ground- and excited-state redox properties**
- ✐ **the presence of adsorbing group**
- ✐ **large spectral overlap with solar emission spectrum**

- **Attaching Group**
- **Steric Effect**
- **Extending the spectral response of the sensitizer**
- **Controlling of the charge recombination**

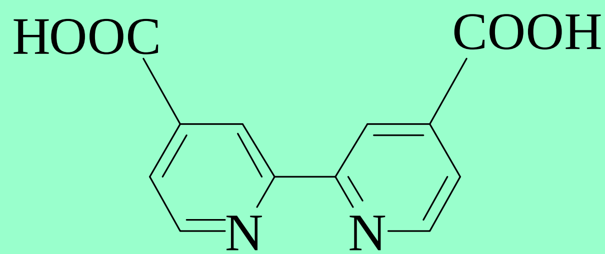
Various types bipyridine ligands with different attaching groups that are being used in solar cell studies



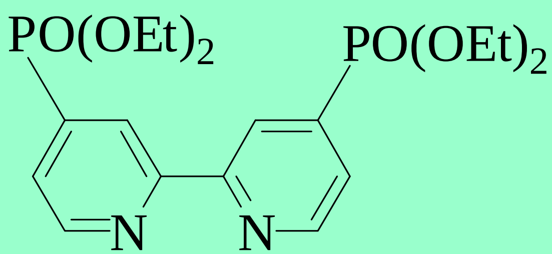
bpy-CO_2Et



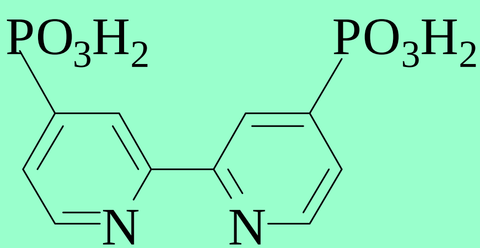
bpy-CH_2OH



bpy-COOH

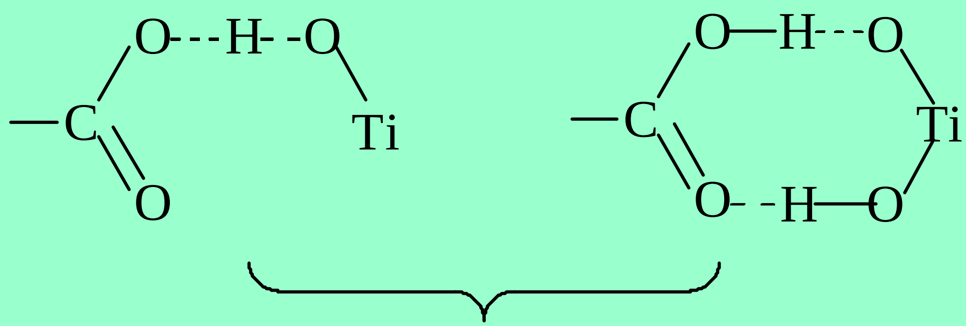


bpy-$PO(OEt)_2$

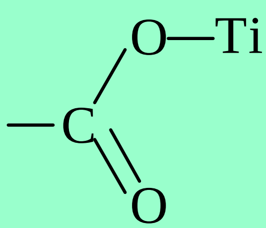


bpy-PO_3H_2

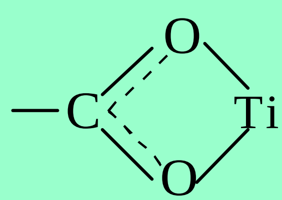
Possible modes of the interactions between the sensitizers and the surfaces of semiconductor oxides



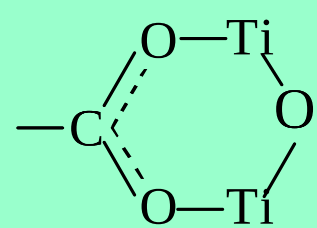
H-bonding



ester forming



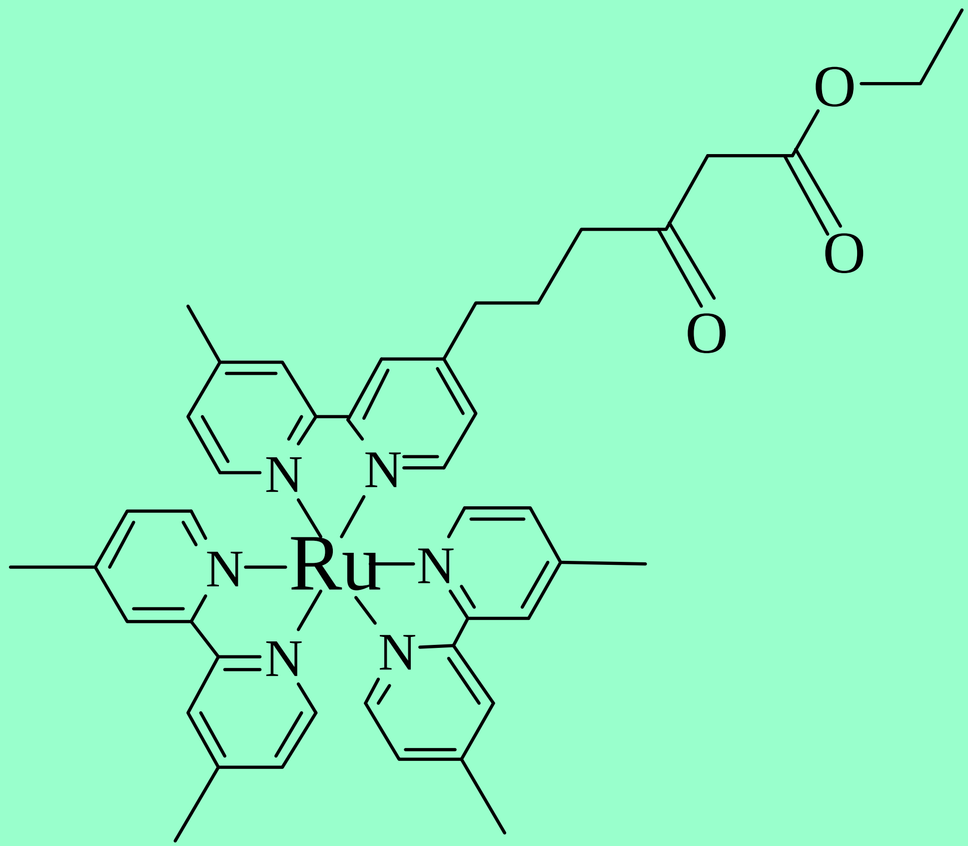
chelating



bridge bonding

Performance of solar cells based on nanocrystalline TiO_2 sensitized by *cis*-$RuL_2(NCS)_2$

L	I_{sc} (mA/cm^2)	V_{oc} (mV)	ff	η%
bpy-CO_2Et	1.8	380	0.47	0.5
bpy-CH_2OH	10	510	0.48	3.8
4,4'-(LL)	18	570	0.41	7.0
bpy-$PO(OEt)_2$	1.6	410	0.44	0.44
bpy-PO_3H_2	6.4	420	0.62	2.6

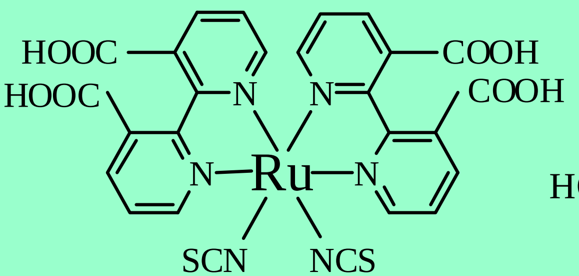


Inorg. Chem. 1996,35 5319-5324

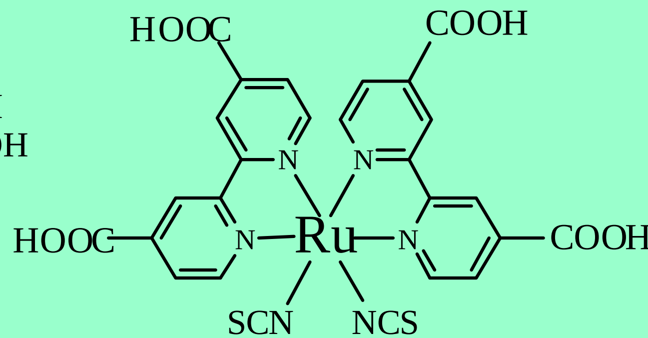
Conclusion

Attaching group could alter the interaction between the sensitizers and surfaces of TiO_2 nanocrystalline electrodes,and good effect of sensitization can only be obtained when the interaction between the sensitizer and surface of semiconductor is strong

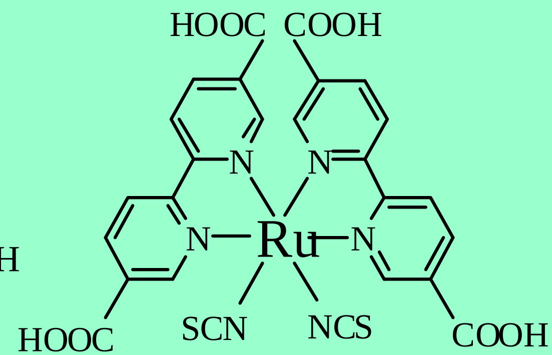
Steric Effect



cis-(NCS)$_2$Ru(3,3¡¯ -LL)$_2$

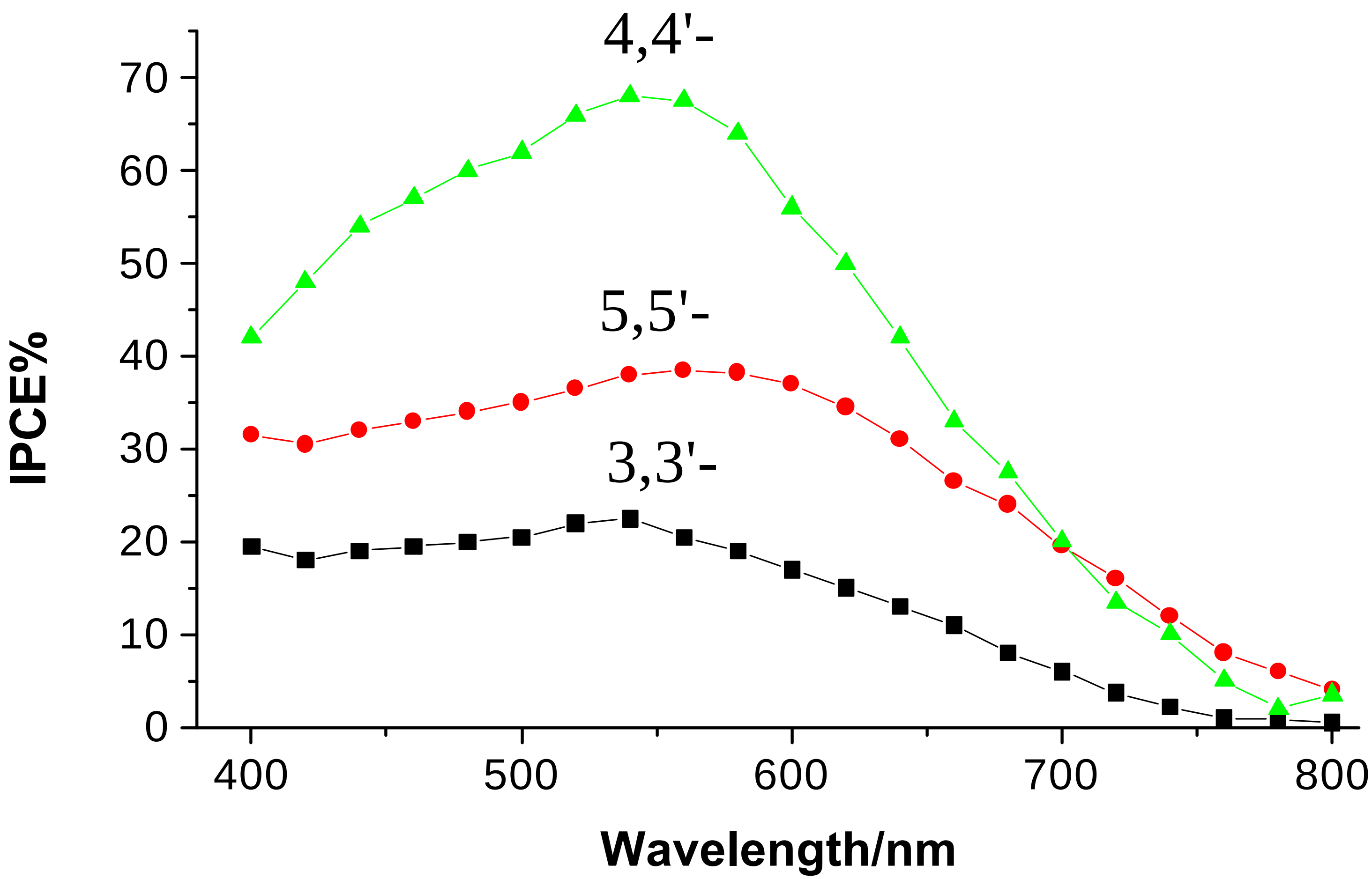


cis-(NCS)$_2$Ru(4,4¡¯ -LL)$_2$



cis-(NCS)$_2$Ru(5,5¡¯ -LL)$_2$

Photocurrent action spectrum for three photosensitizers measured on nanocrystalline TiO_2 solar cells



Absorption, Electrochemical, and Photoelectrochemical Properties

complex	$\lambda_{abs.max}$ (nm)	E_0 (V,vsSCE)	I_{sc} (mA/cm^2)	V_{oc} (V)	max IPCE
3,3’-LL	570	0.87	8.0	0.47	0.213
4,4’-LL	535	0.85	18.4	0.57	0.671
5,5’-LL	580	0.95	7.8	0.49	0.366

$$IPCE(\lambda)=\Phi_{inj}\, LHE(\lambda)\, \eta_c$$

IPCE= incident photo-to-current conversion efficiency for monochromatic radiation, effective quantum yield of the device

LHE=light harvesting efficiency

f_{inj}=charge injection yield

h_C=charge collection efficiency

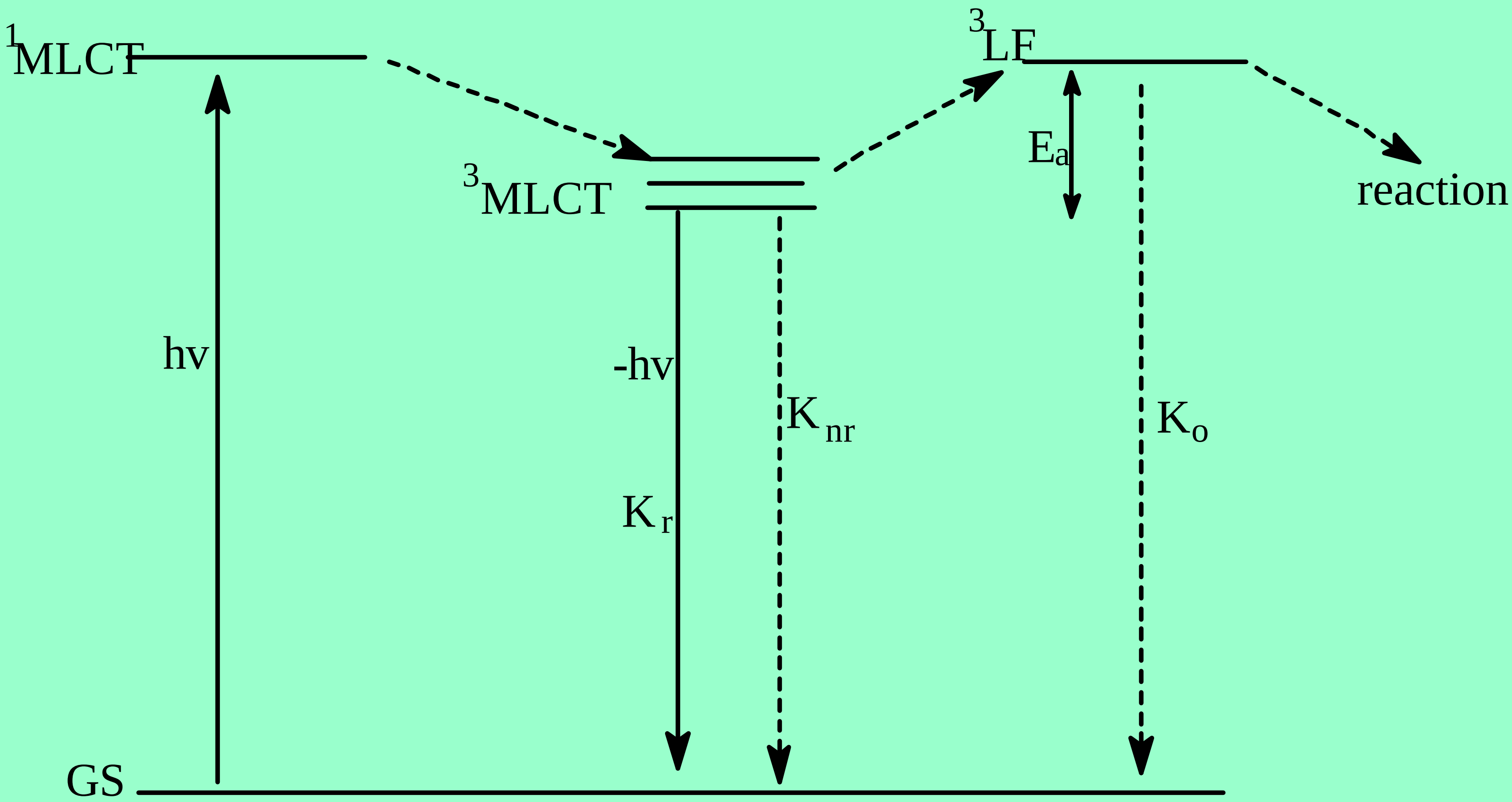
$$\Phi_{inj} = \frac{k_{inj}}{k_r + k_{nr} + k_{inj}}$$

k_{inj}=electron injection rate constant

k_{nr}=nonradiative rate constant

k_r=radiative rate constant

Energy-level diagram showing the excited-state processes occurring in ruthenium polypyridyl compounds



Nonradiative Decay of Excited State

- ✩ **direct deactivation channel**
- ✩ **thermally activated decay path**

Possible explanation for steric effect

- Changes in spatial hindrance of ligand which influence energy level will therefore have an impact on the nonradiative decay of the excited state

- steric factor affects the electric coupling between the surface of nanocrystalline semiconductor and the sensitizers

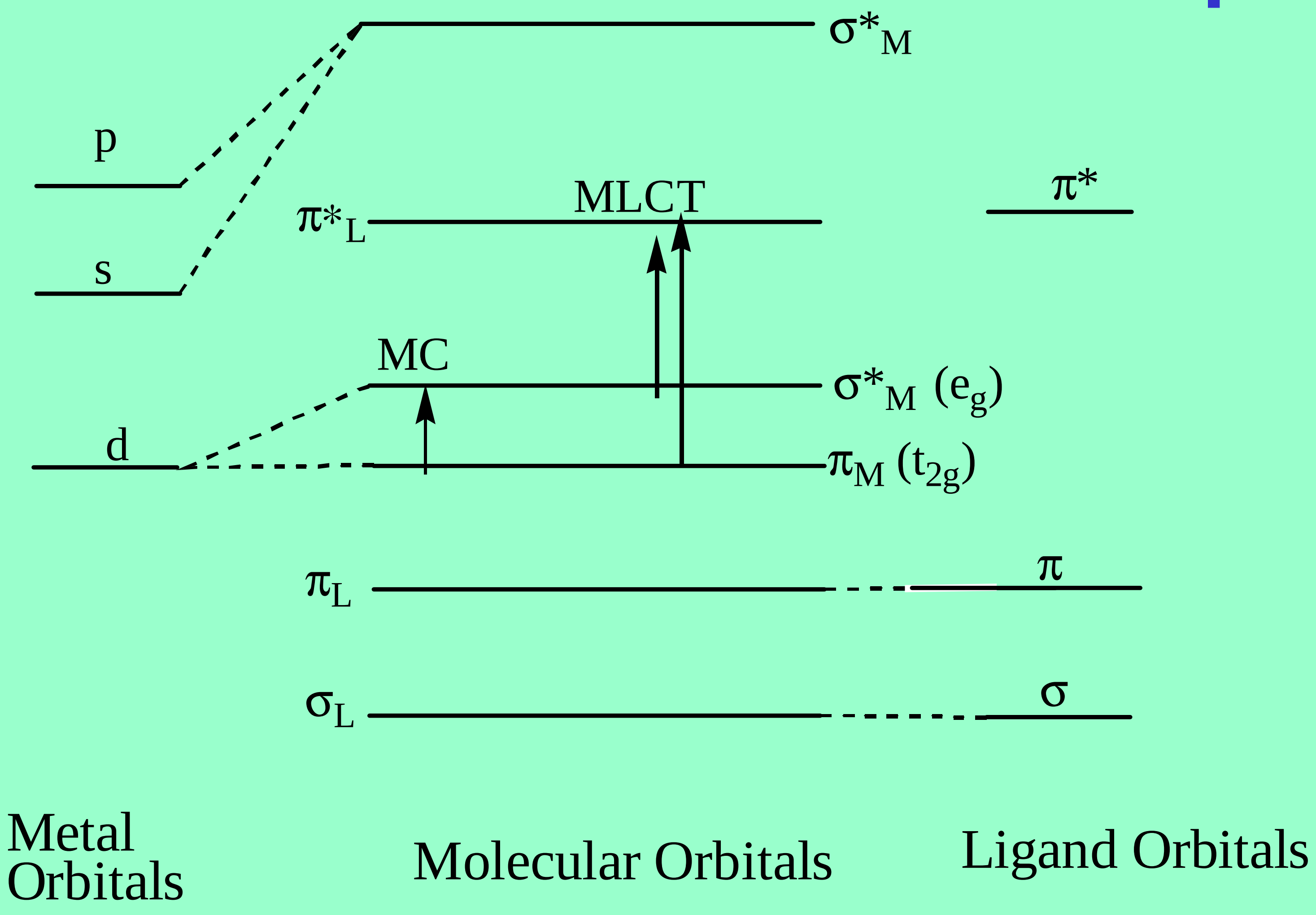
Improvement of efficiency of the dye-sensitized solar cells

- Extending the spectral sensitivity of the dyes towards the red portion of the solar spectrum
- Controlling the rate of charge recombination

Extending MLCT Absorption to the red portion of solar emission

- Synthesis of black dyes
- Co-sensitization

Schematic energy-level diagram for an octahedral transition metal complex



Strategy for Designing of "Black Sensitizer"

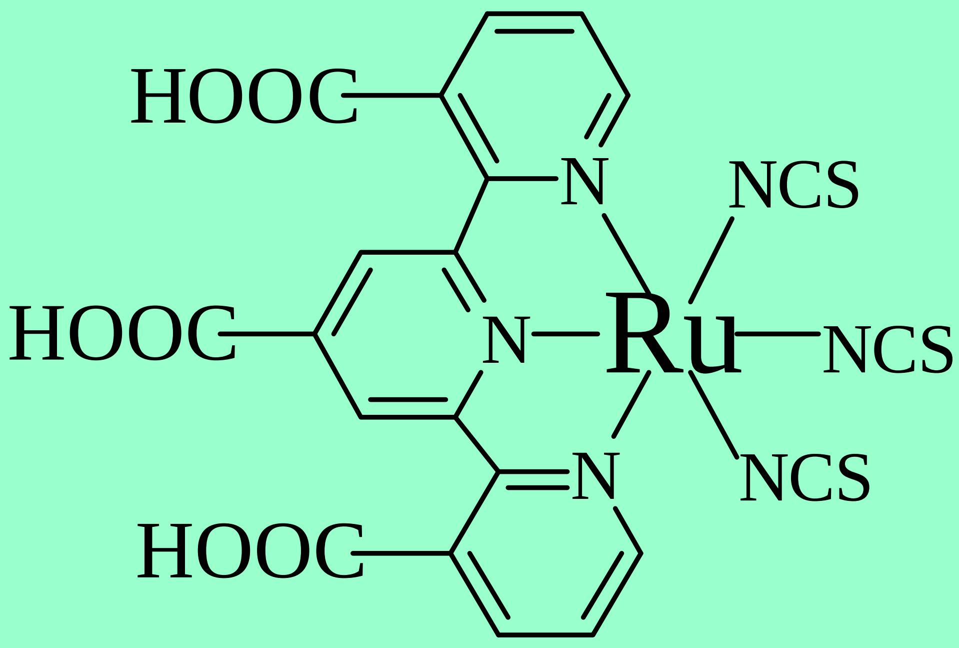
- ✐**Decreasing the energy of the ligand p* orbital**

- ✐**Raising the energy of the metal t_{2g} orbital**

Disadvantages

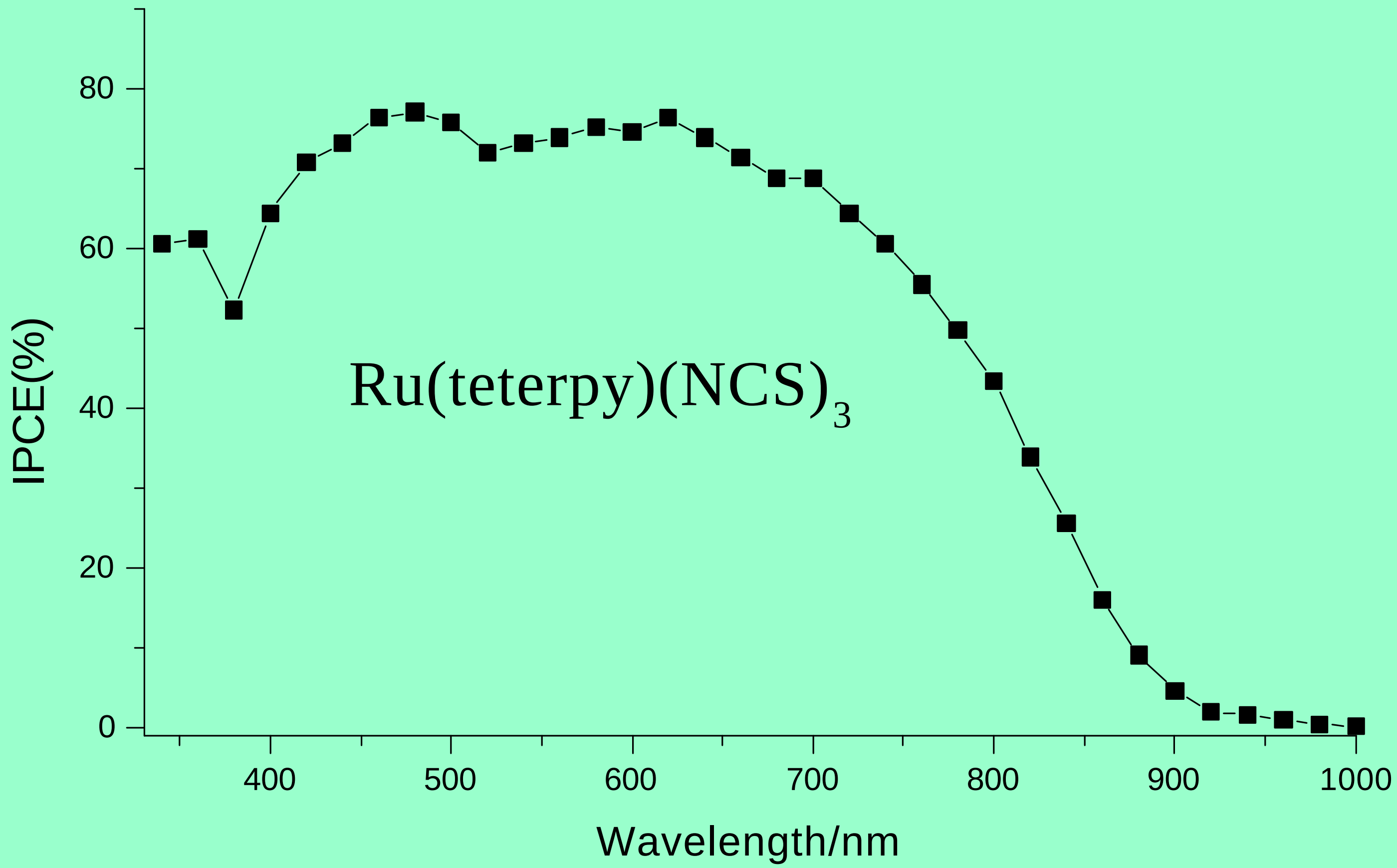
- Stabilization of the p* levels of the diimine ligands can result in a poor interfacial charge separation yield
- Decreasing the metal-based reduction potential can result in sluggish iodide oxidation rates

Structure of the black dye

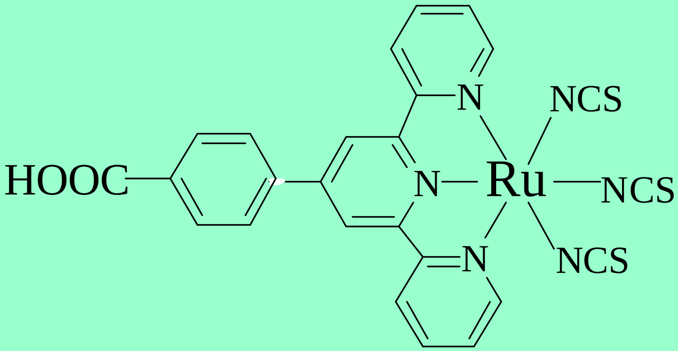


Coordination Chemistry Reviews 1998, 177, 367

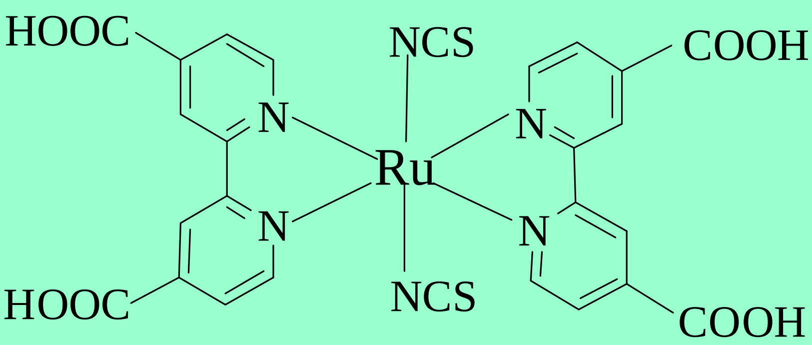
Photocurrent action spectrum of black dye



Novel Black Dyes

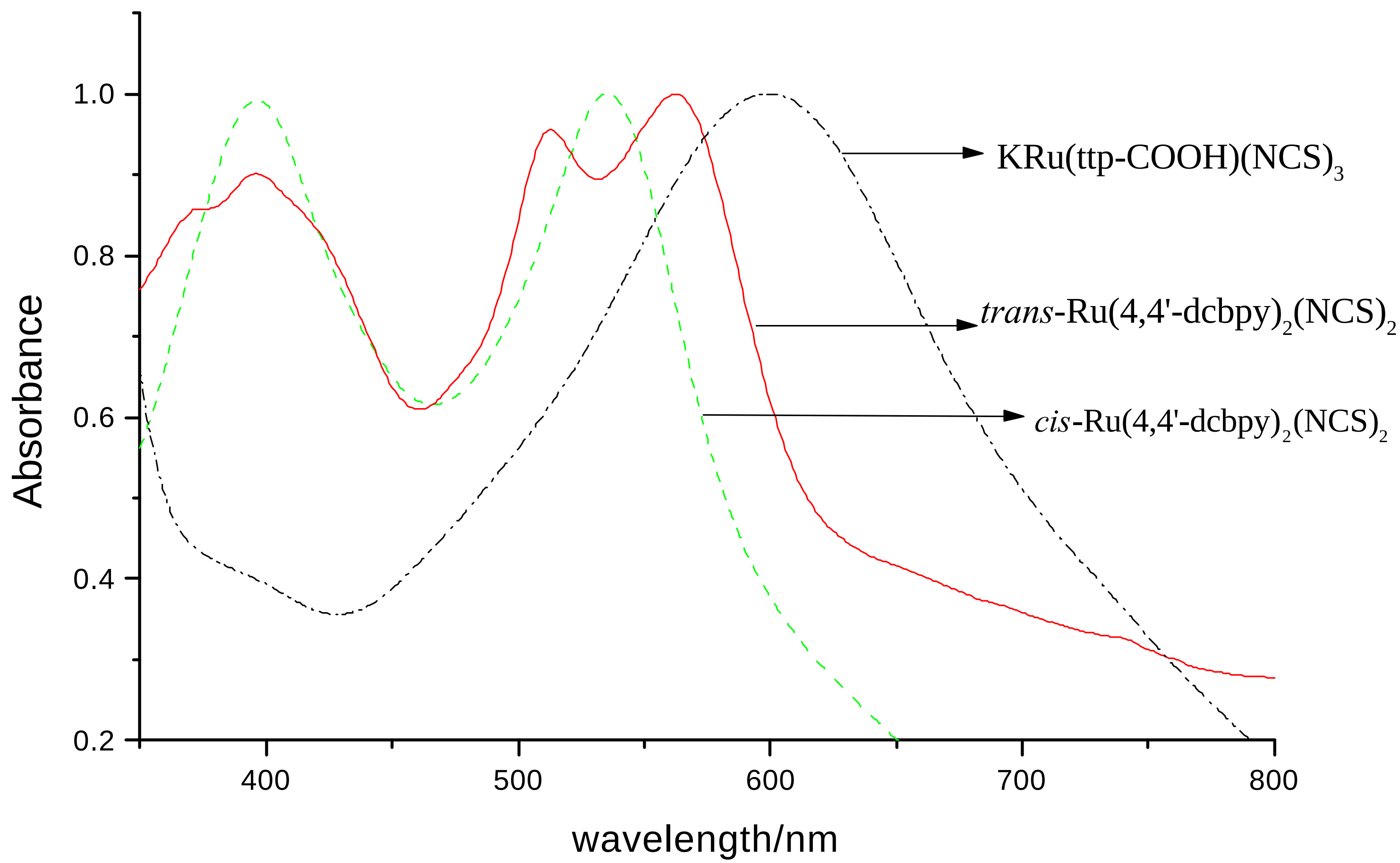


[Ru(*p*-COOH-phenyl-tpy)(NCS)$_3$]$^-$

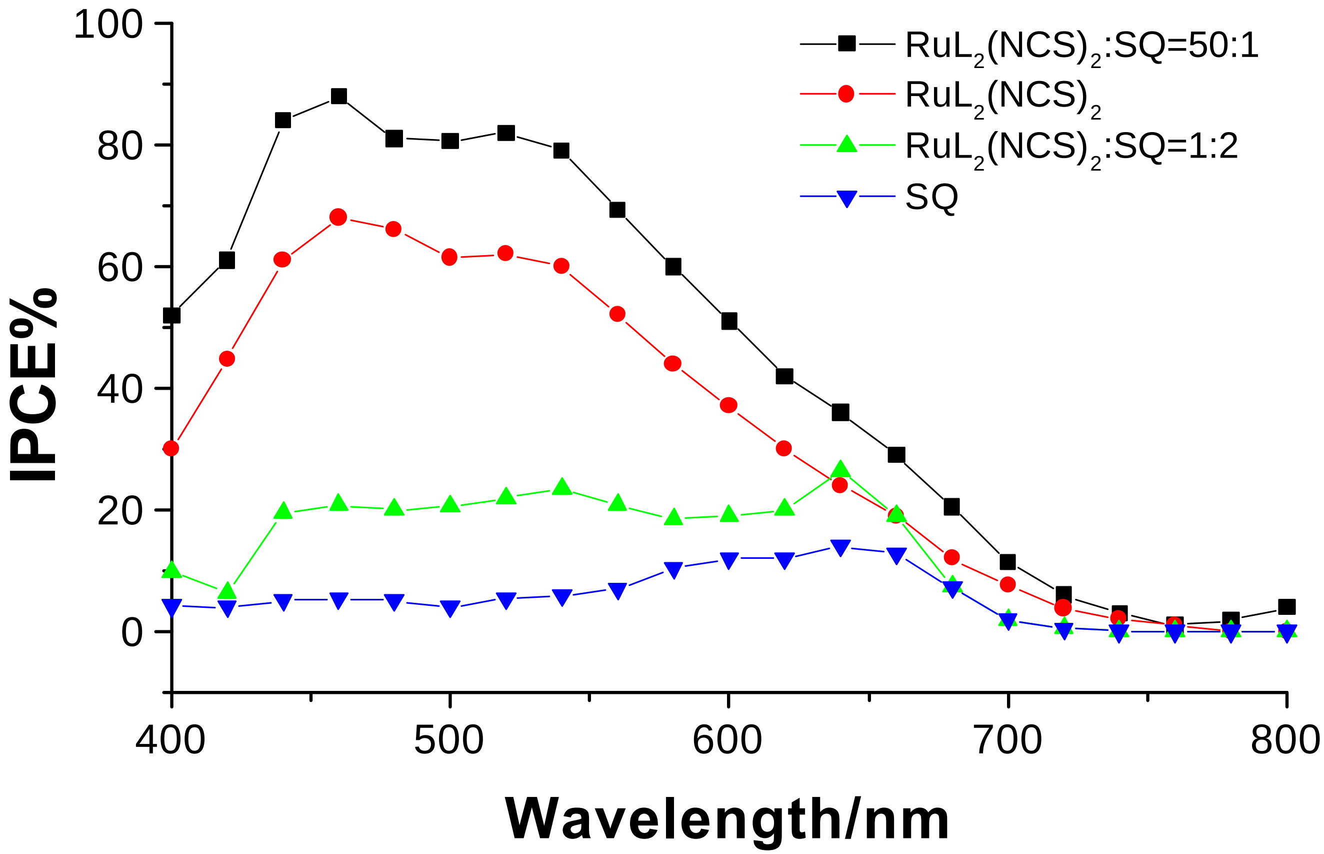


trans-Ru(dcbpy)$_2$(NCS)$_2$

Absorption spectra



Action spectra

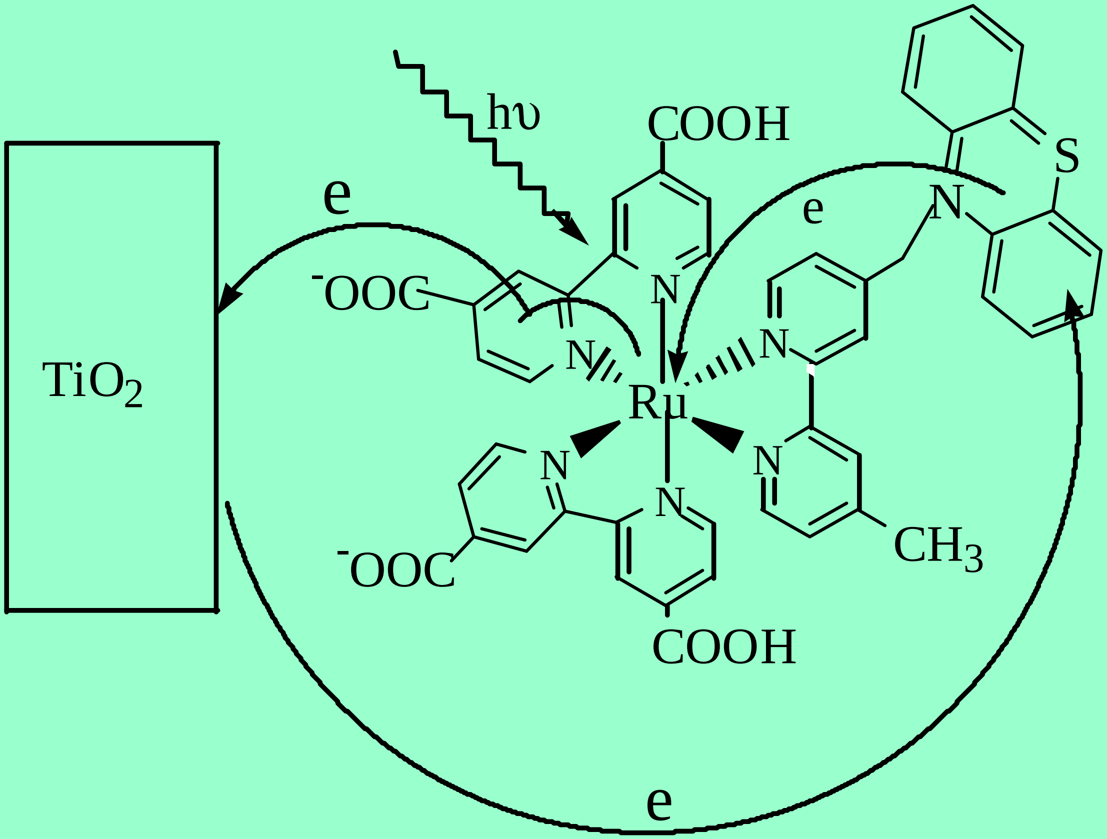


Summary

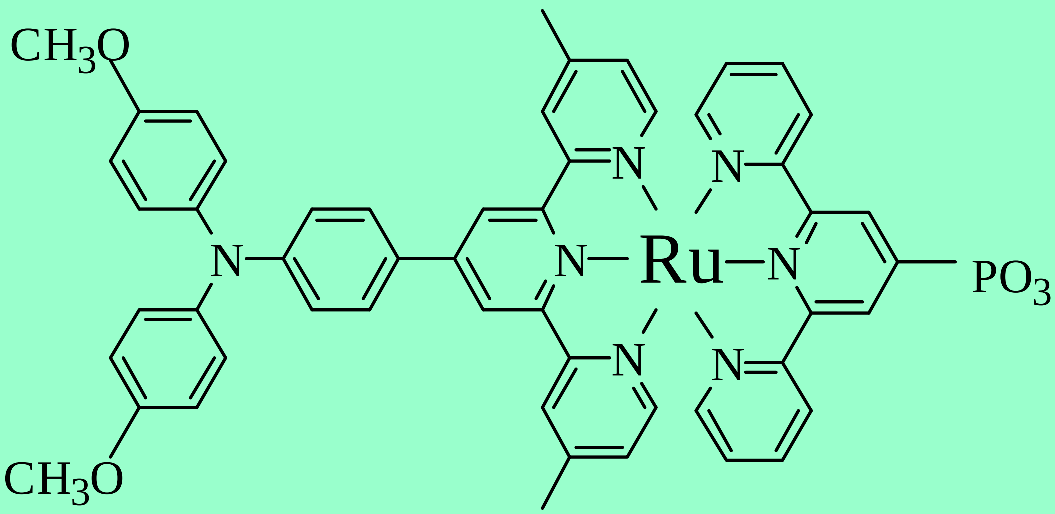
The efficiency can be improved by co-sensitization by utilizing dyes with complimentary absorption bands modified surface to capture the broad spectral output of solar radiation

Approach to increasing photovoltage

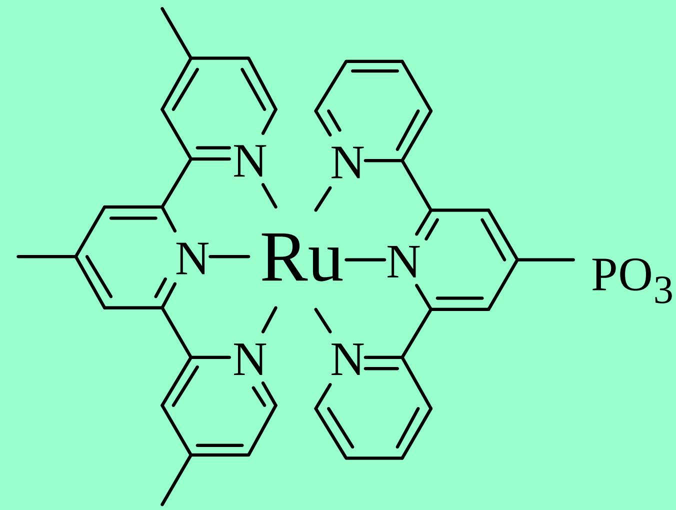
- adding pyridine derivatives to the electrolyte to inhibit recombination of injected electrons with I_3^-
- translating vectorially the hole away from the sensitizer through intramolecular electron transfer



J. Chem. Edu. *1997 P652-656*



$\tau_{1/2}$=30μs V_{OC}=692mV



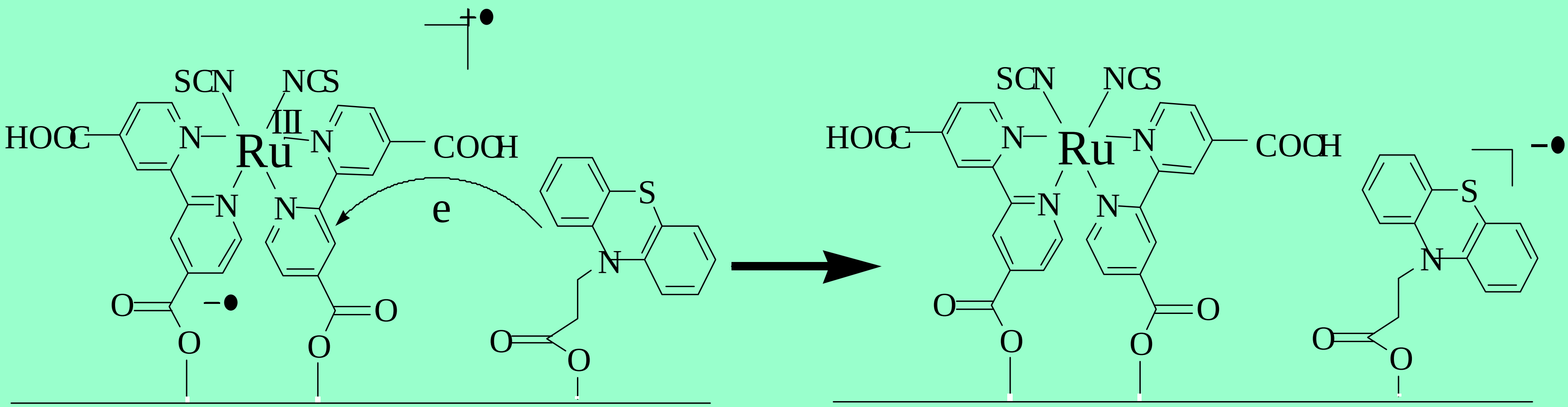
$\tau_{1/2}$=3μs V_{OC}=553mV

J. Am. Chem. Soc. 2000, 122, 2840-2849

Data of treatment with Phenothiazine derivative

	I_{sc} (mA/cm^2)	V_{oc} (mV)	ff (%)
untreated	9.0	610	58
treated	7.7	650	66

Intermolecular electron transfer on the Surface



Summary

Introduction of electron donor could increase the photovoltage and improve the energy conversion efficiency

Conclusion

- **electronic coupling is crucial parameter for efficient photosensitization**
- **electronic coupling can be mediated by the attaching group and steric factor**
- **the efficiency can be improved by co-sensitization**
- **introduction of electron donor can improve the efficiency of solar cell**

Acknowledgements

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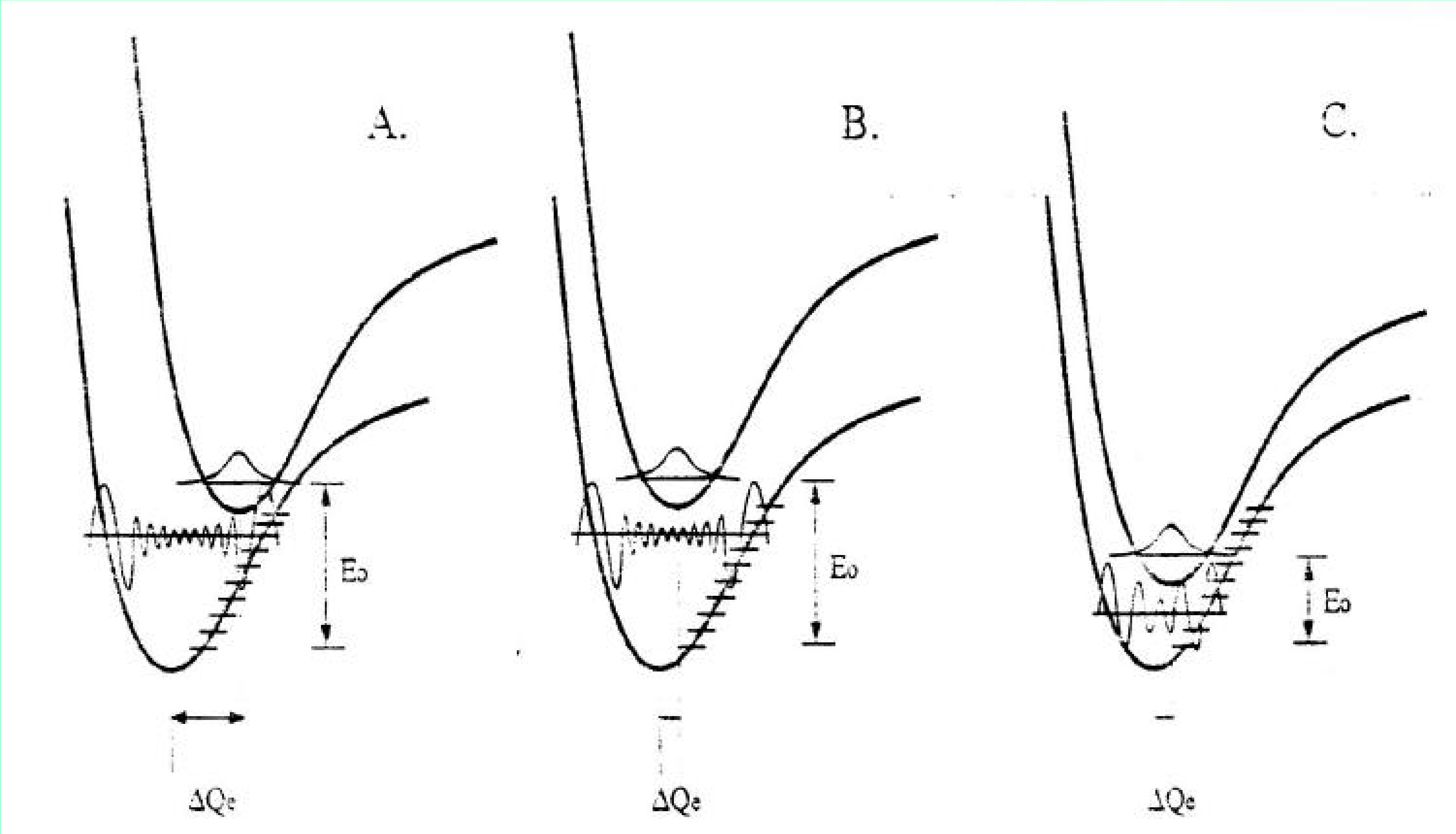
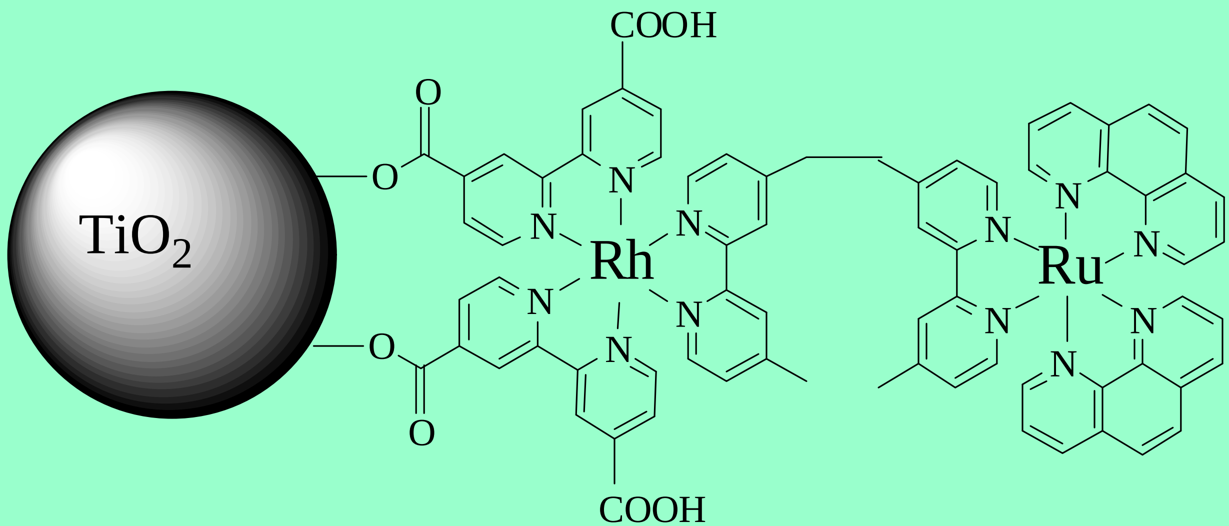
$$k_{nr} \propto \exp(-\frac{\gamma E_0}{\hbar \omega_M}) \qquad (1)$$

$$\gamma = \ln(\frac{E_0}{S_M \hbar \omega_M}) - 1 \qquad (2)$$

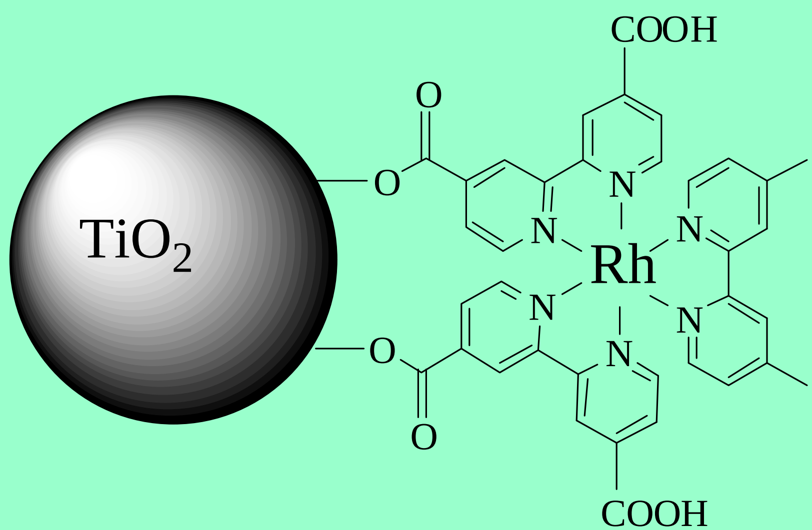
$$S_M = \frac{1}{2}(\frac{M\omega}{\hbar})(\Delta Q_e)^2 \qquad (3)$$

Graphical illustration of the factors influencing vibrational overlap for non-radiative excited-state decay

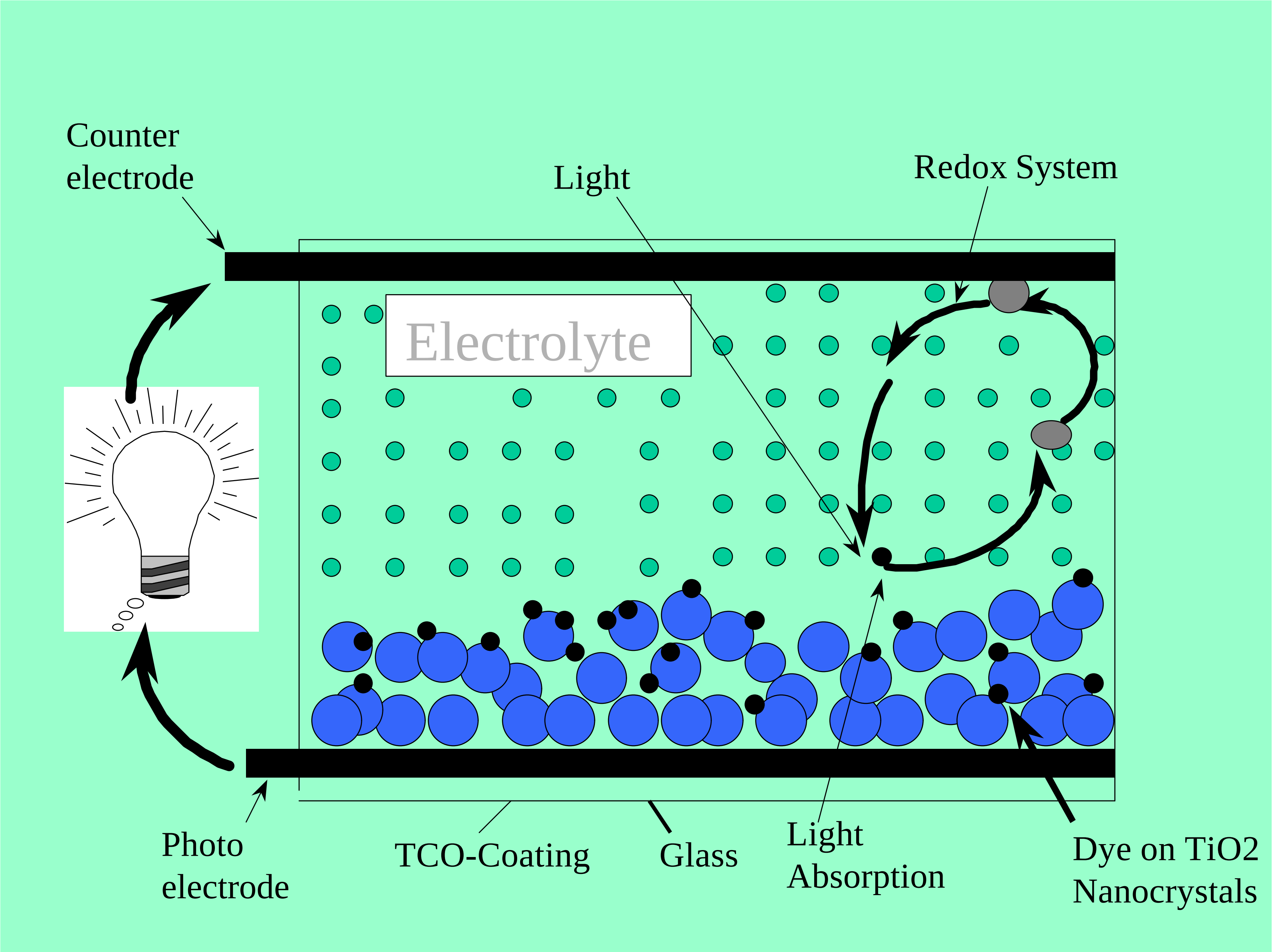




$TiO_2(e^-)$-Rh(II)-Ru(III) $\longrightarrow$ TiO_2-Rh(III)-Ru(II)



$TiO_2(e^-)$-Ru(III) $\longrightarrow$ TiO_2-Ru(II)


Counter electrode
Light
Redox System
Electrolyte
Photo electrode
TCO-Coating
Glass
Light Absorption
Dye on TiO2 Nanocrystals